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– Hydrospheric Environment Analytical Chemistry –

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Scope of Research

(i) Biogeochemistry of trace elements in the hydrosphere: Novel analytical methods are developed for trace metals and their isotopes. Distribution of trace elements in the hydrosphere and their effects on the ecosystem are investigated. The study also covers hydrothermal activity, deep biosphere, and paleocean. (ii) Ion recognition: Novel ligands and ion recognition system are designed, synthesized, and characterized.



KEYWORDS

Marine Chemistry Analytical Chemistry Trace Elements
Stable Isotopes Metal Ion Recognition

Selected Publications

Yang, L.; Nadeau, K.; Meija, J.; Grinberg, P.; Pagliano, E.; Ardini, F.; Grotti, M.; Schlosser, C.; Streu, P.; Achterberg, E. P.; Sohrin, Y.; Minami, T.; Zheng, L.; Wu, J.; Chen, G.; Ellwood, M. J.; Turetta, C.; Aguilar-Islas, A.; Rember, R.; Sarthou, G.; Tonnard, M.; Planquette, H.; Matoušek, T.; Crum, S.; Mester, Z., Inter-Laboratory Study for the Certification of Trace Elements in Seawater Certified Reference Materials NASS-7 and CASS-6, *Anal. Bioanal. Chem.*, **410**, 4469-4479 (2018).

Yang, S.-C.; Zhang, J.; Sohrin, Y.; Ho, T.-Y., Cadmium Cycling in the Water Column of the Kuroshio-Oyashio Extension Region: Insights from Dissolved and Particulate Isotopic Composition, *Geochim. Cosmochim. Acta*, **233**, 66-80 (2018).

Sieber, M.; Conway, T. M.; De Souza, G. F.; Obata, H.; Takano, S.; Sohrin, Y.; Vance, D., Physical and Biogeochemical Controls on the Distribution of Dissolved Cadmium and Its Isotopes in the Southwest Pacific Ocean, *Chem. Geol.* (2018) (in press).

Zheng, L.; Minami, T.; Takano, S.; Minami, H.; Sohrin, Y., Distribution and Stoichiometry of Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb in Seawater Around the Juan de Fuca Ridge, *J. Oceanogr.*, **75**, 669-685 (2017).

Takano, S.; Tanimizu, M.; Hirata, T.; Shin, K. T.; Fukami, Y.; Suzuki, K.; Sohrin, Y., A Simple and Rapid Method for Isotopic Analysis of Nickel, Copper, and Zinc in Seawater Using Chelating Extraction and Anion Exchange, *Anal. Chim. Acta*, **967**, 1-11 (2017).

Inter-laboratory Study for the Certification of Trace Elements in Seawater Certified Reference Materials NASS-7 and CASS-6

Certification of trace metals in seawater certified reference materials (CRMs) NASS-7 and CASS-6 is described (Yang et al., 2018a). At the National Research Council Canada (NRC), column separation was performed to remove the seawater matrix prior to the determination of Cd, Cr, Cu, Fe, Pb, Mn, Mo, Ni, U, V, and Zn, whereas As was directly measured in 10-fold diluted seawater samples, and B was directly measured in 200-fold diluted seawater samples. High-resolution inductively coupled plasma mass spectrometry (HRICPMS) was used for elemental analyses, with double isotope dilution for the accurate determination of B, Cd, Cr, Cu, Fe, Pb, Mo, Ni, U, and Zn in seawater NASS-7 and CASS-6, and standard addition calibration for As, Co, Mn, and V. In addition, all analytes were measured using standard addition calibration with triple quadrupole (QQQ)-ICPMS to provide a second set of data at NRC. Expert laboratories worldwide were invited to contribute data to the certification of trace metals in NASS-7 and CASS-6. Various analytical methods were employed by participants including column separation, co-precipitation, and simple dilution coupled to ICPMS detection or flow injection analysis coupled to chemiluminescence detection, with use of double isotope dilution calibration, matrix matching external calibration, and standard addition calibration. Results presented in this study show that majority of laboratories have demonstrated their measurement capabilities for the accurate determination of trace metals in seawater. As a result of this comparison, certified/reference values and associated uncertainties were assigned for 14 elements in seawater CRMs NASS-7 and CASS-6, suitable for the validation of methods used for seawater analysis. This subject was an international collaborative study with Dr. Zoltán Mester at NRC.

Cadmium Cycling in the Water Column of the Kuroshio-Oyashio Extension Region: Insights from Dissolved and Particulate Isotopic Composition

We measured dissolved and particulate Cd isotopic composition in the water column of a meridional transect across the Kuroshio-Oyashio Extension region in a Japanese GEOTRACES cruise to investigate the relative influence of physical and biogeochemical processes on Cd cycling in the Northwestern Pacific Ocean (Yang et al., 2018b). Located at 30–50°N along 165°E, the transect across the extension region possesses dramatic hydro-

graphic contrast. Cold surface water and a relatively narrow and shallow thermocline characterizes the Oyashio Extension region in contrast to a relatively warm and highly stratified surface water and thermocline in the Kuroshio Extension region. The contrasting hydrographic distinction at the study site provides us with an ideal platform to investigate the spatial variations of Cd isotope fractionation systems in the ocean. Particulate samples demonstrated biologically preferential uptake of light Cd isotopes, and the fractionation effect varied dramatically in the surface water of the two regions, with relatively large fractionation factors in the Oyashio region. Based on the relationship of dissolved Cd concentrations and isotopic composition, we found that a closed system fractionation model can reasonably explain the relationship in the Kuroshio region. However, using dissolved Cd isotopic data, either a closed system or steady-state open system fractionation model may explain the relationship in the surface water of the Oyashio region. Particulate $\delta^{114/110}\text{Cd}$ data further support that the surface water of the Oyashio region matches a steady-state open system model more closely. Contrary to the surface water, the distribution of potential density exhibits comparable patterns with Cd elemental and isotopic composition in the thermocline and deep water in the two extension regions, showing that physical processes are the dominant forcing controlling Cd cycling in the deep waters. The results demonstrate that Cd isotope fractionation can match either a closed or open system Rayleigh fractionation model, depending on the relative contribution of physical and biogeochemical processes on its cycling. This subject was an international collaborative study with Dr. Tung-Yuan Ho at Academia Sinica, Taiwan.

Yang, L. *et al.*, Inter-Laboratory Study for the Certification of Trace Elements in Seawater Certified Reference Materials NASS-7 and CASS-6, *Anal. Bioanal. Chem.*, **410**, 4469-4479 (2018).

Yang, S.-C.; Zhang, J.; Sohrin, Y.; Ho, T.-Y., Cadmium Cycling in the Water Column of the Kuroshio-Oyashio Extension Region: Insights from Dissolved and Particulate Isotopic Composition, *Geochim. Cosmochim. Acta*, **233**, 66-80 (2018).



Figure 1. Dr. Tung-Yuan Ho at Lake Shinji.